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Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity

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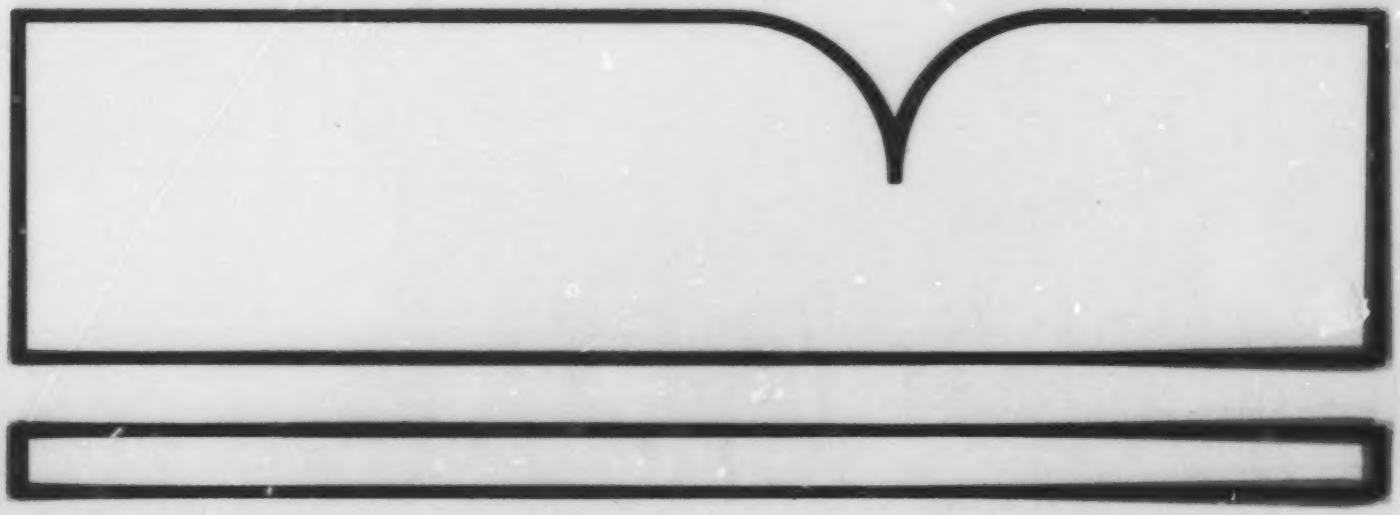

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16. ABSTRACT

Vapor sorption isotherms on dry Woodburn soil at 20-30° C were determined for benzene, chlorobenzene, p-dichlorobenzene, m-dichlorobenzene, 1,2,4-trichlorobenzene, and water as single vapors and for benzene, m-dichlorobenzene, and 1,2,4-trichlorobenzene as functions of relative humidity(RH). Isotherms for all compounds on dry soil samples are distinctively nonlinear, with water showing the greatest capacity. Water vapor sharply reduced the sorption capacities of organic compounds with the dry soil; on water-saturated soil, the reduction was about 2 orders of magnitude. The markedly higher sorption on organic vapors at subsaturation humidities is attributed to adsorption on the mineral matter, which predominates over the simultaneous uptake by partition into the organic matter. At about 90% RH, the sorption capacities of organic compounds become comparable to those in aqueous systems. The effect of humidity is attributed to adsorptive displacement by water of organics adsorbed on the mineral matter. A small residual uptake is attributed to the partition into the soil-organic phase that has been postulated in aqueous systems. The results are essentially in keeping with the model that was previously proposed for sorption on the soil from water and from organic solvents.

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JOURNAL ARTICLE

Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity

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■ Vapor sorption isotherms on dry Woodburn soil at 20–30 °C were determined for benzene, chlorobenzene, *p*-dichlorobenzene, *m*-dichlorobenzene, 1,2,4-trichlorobenzene, and water as single vapors and for benzene, *m*-dichlorobenzene, and 1,2,4-trichlorobenzene as functions of relative humidity (RH). Isotherms for all compounds on dry soil samples are distinctively nonlinear, with water showing the greatest capacity. Water vapor sharply reduced the sorption capacities of organic compounds with the dry soil; on water-saturated soil, the reduction was about 2 orders of magnitude. The markedly higher sorption of organic vapors at subsaturation humidities is attributed to adsorption on the mineral matter, which predominates over the simultaneous uptake by partition into the organic matter. At about 90% RH, the sorption capacities of organic compounds become comparable to those in aqueous systems. The effect of humidity is attributed to adsorptive displacement by water of organics adsorbed on the mineral matter. A small residual uptake is attributed to the partition into the soil-organic phase that has been postulated in aqueous systems. The results are essentially in keeping with the model that was previously proposed for sorption on the soil from water and from organic solvents.

Introduction

In earlier studies, we dealt with the soil sorption of nonionic organic compounds in water and in organic solvents (*1–6*). The sorption capacities of solutes on a given soil were linear with solute concentrations in water and were nonlinear and much higher in nonpolar organic solvents. These characteristics were interpreted by the assumption that the soil behaved as a dual sorbent, in which the mineral matter functioned as a conventional solid adsorbent and the organic matter as a partition medium. The linear isotherms in aqueous systems were attributed to partition in the organic matter, with concomitant suppression by water of adsorption on the mineral matter (*1–5*). The nonlinear isotherms from the organic solvents (which minimize partition in the organic matter) were attributed to adsorption on the mineral matter, on which the specific interactions of adsorbate polar groups reduced competition by the organic solvents (*2, 5, 6*).

We here consider the sorption behavior of organic vapors on one of the earlier studied soils, both as single vapor components and as functions of relative humidity. This study supplements earlier sorption studies in aqueous systems by enabling us to vary the chemical potential of water and thereby to study its adsorptive displacement effect in greater detail to simulate the sorption of organic compounds by natural soils under the wide variation in humidity that they may experience.

The studies have been carried out for some organic compounds on a soil sample (Woodburn soil) that was used in the earlier study on sorption from water solution. The vapor-phase sorption data determined here are compared with the corresponding data derived from aqueous systems.

Experimental Section

The soil uptake of selected organic compounds from the vapor phase at varying humidities was carried out by a dynamic-equilibrium sorption apparatus in a constant-temperature room (Figure 1). The test compound was blended with quartz sand and placed in a glass column (2.5 in. i.d. × 14 in.), which served as the chemical vapor generator when N_2 gas was passed from the bottom of the column. The column was connected to the vapor-mixing chamber at the top by a standard 71/60 taper joint. A separate glass column (1.5 in. i.d. × 16 in.), filled with water and cut pieces of Teflon tubing, served as a moisture generator, by passing dry N_2 gas from the bottom of the column. The top of this moisture generator column was connected to the vapor-mixing chamber by a standard 24/40 taper joint. Exit vapors from these two columns (controlled by valves V2 and V3) were combined and mixed with a third stream of makeup dry N_2 gas (controlled by valve V1) at the vapor-mixing chamber to produce a final stream of vapor mixture of test chemical and moisture in N_2 gas. This final vapor mixture was then brought in contact with the soil sample placed in a rotating flask to attain dynamic equilibria between vapors and soil.

Total gas-flow rates out of the mixing chamber were maintained in the range 100–250 mL/min in normal runs. By proper control of the flow rate of each column saturator and that of the makeup gas, steady vapor concentrations at a fixed relative humidity could be obtained. A heating tape was wrapped around the sand column, when needed, to increase the vapor concentration. Amounts of the organic vapor sorbed by soil at varying concentrations at a fixed humidity were determined by extraction of the soil. The resulting data were used to make an isotherm plot.

Vapor concentrations and relative humidities were measured prior to placing soil samples into the rotating flask. To do this, the total gas flow rate was first measured by a soap-bubble flow meter. Relative humidity (RH) was determined subsequently by inserting a glass tube containing 2–3 g of Dehydrite (magnesium perchlorate) at the end of the mixing chamber to trap the moisture. The concentration of water vapor was calculated on the basis of weight gain of magnesium perchlorate, total gas flow rate, and trapping time. Vapor concentrations of the test compound were determined by extracting the vapor at the outlet of the mixing chamber with a gas impinger (micro-bubbler, Ace Glass Co.) filled with hexane (20 mL) as the extracting solvent. To ensure steady flows of water and chemical vapor, these measurements were repeated as many times as needed.

When the vapor system reached a steady-state condition, the soil sample was placed in the (rotating) sample flask. After the sorption was measured for one combination of vapor concentration and RH, the vapor concentration was then varied by adjusting the flow rate through value V2, while the RH was kept unchanged. This was done by adjusting the flow rate of the makeup gas to compensate for the variation of gas flow to the chemical-vapor gener-

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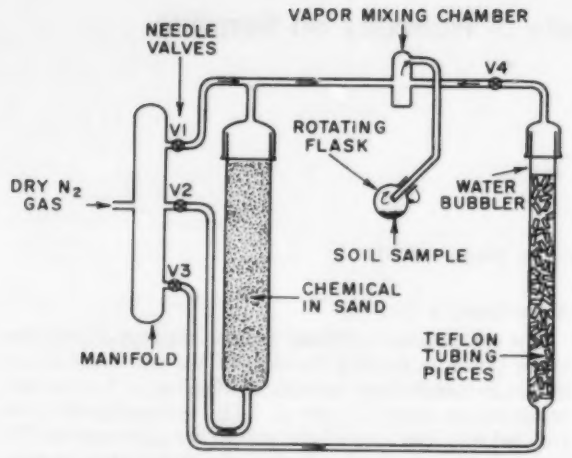

Figure 1. Schematic diagram of the dynamic vapor-sorption apparatus.

ator. This procedure reduced the time involved for conditioning the entire vapor system. With the control as described, the error in vapor concentration and RH is generally within ±3%. However, some difficult was experienced in maintaining constant RH above 85%, while the vapor concentration of the compound was varied; the resulting error was about ±5% for both organic and water vapors. To obtain 0% RH in the experiment, valves V3 and V4 were closed, and a column of Drierite ($CaSO_4$) was inserted to the end of the mixing chamber to remove residual moisture in the system.

To thoroughly mix the soil sample and to maximize the exposure of the soil to vapors, four indentations were made in the sides of the rotating sample flask. These indentations broke up the lumps of the soil, promoting exposure of the soil to vapors. Normally, an exposure time of about 4 h was sufficient for establishing the sorption equilibrium. The contact time was about 8 h in most runs.

The uptake of *m*-dichlorobenzene and water as single-component vapors by dry soil samples was also measured by using a static equilibrium-sorption apparatus described elsewhere (*7*) (this work was carried out by Professor P. J. Reucroft, Department of Materials Science, University of Kentucky, Lexington, KY). This method could only study the uptake of single vapors; the result was taken as a reference to check the precision of the isotherms of single vapors determined by the dynamic-sorption apparatus. Isotherms of *m*-dichlorobenzene on dry soil (0% RH) determined by both types of apparatus were within 5% in weight of soil uptake. The sorption isotherm of water in this report was based on results derived from the static-sorption apparatus, because steady and accurate humidities at RH <20% by using the dynamic-sorption apparatus were difficult to maintain and because water uptake was very sensitive at low RH.

The Woodburn soil (60/80 mesh fraction) used in this study was from the same batch employed in the previous study on the uptake of organic compounds from water (*4*); the composition of the soil on a dry-weight basis was 1.9% organic matter, 9% sand, 68% silt, and 21% clay. X-ray diffraction indicated that kaolinite and mica were the predominant clay types. Soil samples were oven-dried at 140 °C for 48 h to remove moisture and then stored in a vacuum desiccator before being placed in the sample flask. Samples treated in this manner were considered to be "dry". Expectably, samples dried at this temperature would still retain a small amount of water that is tightly associated with soil minerals. This amount was not determined, and we assumed that it was not significant. The air-dried Woodburn soil contained about 2.5% moisture.

The test organic compounds (benzene, chlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene, and 1,2,4-trichlorobenzene) were all reagent-grade from Aldrich Chemical Co. and were used as received. Except for *p*-dichlorobenzene, the sorption isotherms of the other compounds from aqueous solution on Woodburn soil have been reported in the earlier study (*4*). Following the vapor–soil equilibrium, the soil was removed and extracted for the test compound by a mixture of acetone and hexane (1:1 volume ratio). The recovery of all compounds by this solvent mixture was greater than 97%. The extract was further diluted with hexane to appropriate concentrations for analysis. Chlorinated compounds were analyzed by a gas chromatograph equipped with a ^{63}Ni electron-capture detector, using a 2-mm i.d. × 6 ft glass column packed with 6% SE 30 on Gas Chrom Q 60/80 mesh. Benzene was analyzed by a Cary 11 UV spectrophotometer.

Results and Discussion

Figures 2–6 show the equilibrium isotherms of vapor sorption on Woodburn soil. Isotherms are plotted as milligrams taken up per gram of whole soil (Q) vs. the relative vapor concentration of the compound (P/P^0), where P is the equilibrium partial pressure and P^0 is the saturation vapor pressure of the compound at the system temperature. The use of P/P^0 in the isotherm plot normalizes the activity (or chemical potential) of each compound with respect to its own pure state. This normalization permits a direct comparison between uptakes of different compounds from the vapor phase and also between uptakes of the same compounds from liquid and vapor phases; in aqueous systems, the isotherms are normalized by the relative concentration (C_e/C_s) (where C_e is the equilibrium concentration and C_s is the solubility of the compound). The P^0 values for the compounds studied are taken from the literature (*8*): benzene, 74.0 mmHg (20 °C); chlorobenzene, 10.7 mmHg (20 °C); *m*-dichlorobenzene, 1.67 (20 °C) and 3.00 mmHg (30 °C); 1,2,4-trichlorobenzene, 0.315 (20 °C) and 0.600 mmHg (30 °C); water, 22.1 mmHg (23.8 °C). The P^0 value of *p*-dichlorobenzene at 20 °C (0.65 mmHg) was determined experimentally by analyzing the concentration of the saturated vapor from the chemical-vapor generator. Figure 7 compares the vapor uptake of *m*-dichlorobenzene and 1,2,4-trichlorobenzene by Woodburn soil (in micrograms per gram of soil) at 90% RH with the corresponding uptake from water at 20 °C.

Figure 2 shows the isotherms on dry Woodburn soil at 20 °C for benzene, chlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene, 1,2,4-trichlorobenzene, and water (23.8 °C). All isotherms show a steep rise at low P/P^0, followed by a slower rise at intermediate P/P^0, and then by another sharp rise as P/P^0 approaches 1. The shape of the isotherms corresponds to the Brunauer type-II adsorption, which is characteristic of vapor condensation to form multilayer adsorbates. Note that the isotherms with dry soil are highly nonlinear, in sharp contrast to the linearity of isotherms in aqueous systems, and with markedly greater capacities. For instance, the maximum capacity of *m*-dichlorobenzene with dry Woodburn soil is about 45 mg/g of soil, which is about 100 times the limiting uptake of the compound by the same soil from water (i.e., at $C_e/C_s = 1$). These differences indicate a powerful suppression by water of organic vapor adsorption on soil minerals, which is what one expects for adsorption on mineral adsorbents.

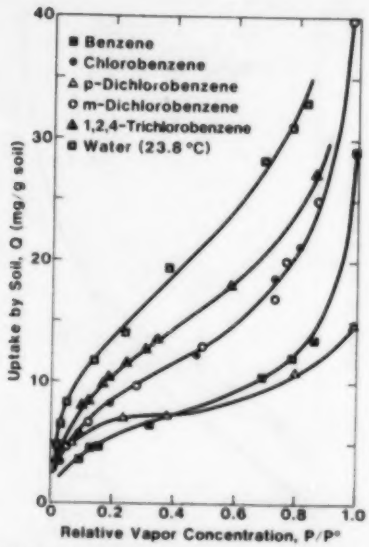

Figure 2. Uptake of organic vapors and moisture by dry Woodburn soil at 20 °C vs. relative vapor concentration.

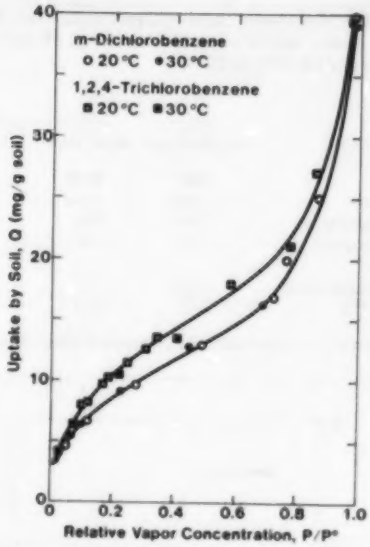

Figure 3. Vapor uptake of *m*-dichlorobenzene and 1,2,4-trichlorobenzene by dry Woodburn soil at 20 and 30 °C.

The capacities of vapor uptake by dry Woodburn soil in Figure 2 are comparable to those of ethylene dibromide (EDB) vapor uptake by various soils and minerals as reported by Call (*9*) and Jurinak (*10*). In Call's study, the EDB uptake by dry soils at $P/P^0 \simeq 0.50$ ranged from approximately 10 mg/g for Field Station soil (7.4% clay and 4.2% organic matter) to 55 mg/g for Boston Silt (46% clay and 4.6% OM), largely in proportion to clay content rather than organic matter content. Jurinak studied the vapor adsorption of EDB by different types of pure clays and the effect of cations associated with clays. At $P/P^0 = 0.90$, amounts of EDB adsorbed by calcium illite, calcium montmorillonite, and calcium kaolinite were approximately 180, 170, and 90 mg/g, respectively, and a significant variation of EDB adsorption was found among Na, Ca, and Mg-exchanged montmorillonites due to variations of BET surface areas. Although uptake capacities would obviously be different between soils because of differences in mineral types and compositions according to these analyses, the results from Figures 2 and 7 of the present study clearly reveal the dominant effect of mineral adsorption with dry Woodburn soil.

The high water uptake by dry Woodburn soil appears to be associated with strong polar interactions of water with polar minerals (*2–4*). Sorption capacities are significantly lower for organic compounds that are not strong wetting agents on polar mineral surfaces. The increasing uptake from benzene to the relatively more polar chlorobenzene, *m*-dichlorobenzene, and 1,2,4-trichlorobenzene also indicates the effect of polarity on mineral adsorption. Relative sorption capacities of organic vapors at low P/P^0 follow the order of 1,2,4-trichlorobenzene > *m*-dichlorobenzene ≃ *p*-dichlorobenzene ≃ chlorobenzene > benzene, roughly in proportion to the number of chlorines in the molecule. At high P/P^0, *p*-dichlorobenzene shows markedly lower uptake than *m*-dichlorobenzene and other compounds. The difference in uptake between *m*-dichlorobenzene and *p*-dichlorobenzene at high P/P^0 occurs presumably because *p*-dichlorobenzene is a solid at room temperature (mp 54 °C), whereas *m*-dichlorobenzene and other compounds are liquids. The inability of a solid adsorbate to form a compact multilayer phase on mineral surfaces would thus lead to a lower capacity compared to those for liquids at high P/P^0. For example, solid adsorbates have been noted to show lower limiting capacities on activated carbon, presumably because of inefficient packing (*11*, *12*).

The fact that adsorption on minerals is enhanced by adsorbate polarity makes water a powerful competitor to displace (nonionic) organic solutes from soil minerals in aqueous systems. The importance of polar interactions in mineral adsorption is also illustrated by the significantly higher uptake of the more-polar parathion than the less-polar lindane from hexane on dry (Woodburn) soil (*6*). This feature is in sharp contrast to purely physical (London-force) adsorption, which is frequently exhibited by activated carbon, where the polarity effects are relatively unimportant; in this case, water is a weak adsorbate, allowing effective adsorption of organic solutes from water (*11*).

Figure 3 shows a comparison of the 20 and 30 °C isotherms of *m*-dichlorobenzene and 1,2,4-trichlorobenzene on dry Woodburn soil in a normalized plot. The coincidence of two isotherms at 20 and 30 °C at $P/P^0 > 0.05$ is evidence that the heats of (mineral) adsorption are essentially the same as the heats of vapor condensation. That is

$$\Delta\bar{H}_Q \simeq -\Delta\bar{H}_v \qquad (1)$$

where $\Delta\bar{H}_Q$ is the (molar) isosteric heat of adsorption at capacity Q and $\Delta\bar{H}_v$ is the heat of vaporization of the compound. The $\Delta\bar{H}_v$ value, calculated by the Clausius–Clapeyron equation using vapor pressure data (*8*), is 10.6 kcal/mol for *m*-dichlorobenzene and 11.7 kcal/mol for 1,2,4-trichlorobenzene. The proximity of $\Delta\bar{H}_Q$ to $-\Delta\bar{H}_v$ at $P/P^0 > 0.05$ is commonplace in adsorption, which is taken as a basic assumption in the BET adsorption theory with adsorbates approaching and exceeding the monolayer capacity (whereas the heat of adsorption below monolayer is considered to be greater than the heat of vapor condensation).

The monolayer adsorption capacity (Q_m) and the molar heat of adsorption ($\Delta\bar{H}_m$) at $Q \leq Q_m$ for each adsorbate on dry Woodburn soil can be determined according to the BET equation (*13*):

$$\frac{x}{Q(1-x)} = \frac{(C-1)x}{CQ_m} + \frac{1}{CQ_m} \qquad (2)$$

Table I. BET Monolayer Adsorption Capacities (Q_m) and Associated Molar Adsorption Heats ($\Delta\bar{H}_m$) of Adsorbates on Dry Woodburn Soil at 20 °C

compound	Q_m, mg/g of soil	$\Delta\bar{H}_v$,[a] kcal/mol	$-(\Delta\bar{H}_m + \Delta\bar{H}_v)$, kcal/mol
benzene	5.57	8.09	1.52
chlorobenzene	7.53	9.43	1.82
m-dichlorobenzene	7.42	10.6	1.86
p-dichlorobenzene (solid)	5.54	15.0	2.54
1,2,4-trichlorobenzene	9.53	11.7	1.93
water (23.8 °C)	11.7	10.3	2.14

[a] Molar heats of vaporization determined from vapor pressure data (*8*).

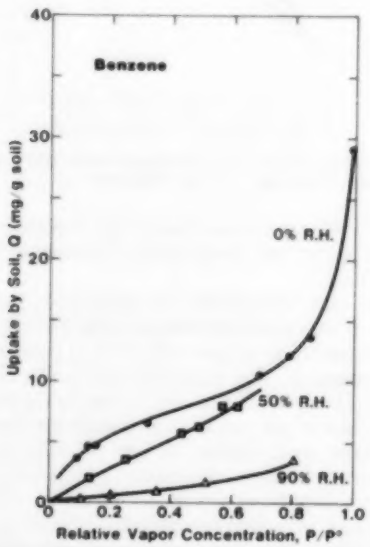

Figure 4. Vapor uptake of benzene by Woodburn soil at 20 °C as a function of relative humidity.

in which $x = P/P^0$, Q_m is the monolayer capacity of adsorbate on soil minerals (mg/g), and C is related to the net molar heat of adsorption at $Q \leq Q_m$ by

$$-\ln C \simeq (\Delta\bar{H}_m + \Delta\bar{H}_v)/(RT) \quad (3)$$

where R is the gas constant and T is the system temperature. By eq 2, a plot of $x/[Q(1-x)]$ vs. x should yield a straight line, with a slope of $(C-1)/(CQ_m)$ and an intercept of $1/(CQ_m)$, from which Q_m and C can be determined. Data in Figure 2 give an excellent fit of eq 2 over the range $P/P^0 = 0.05$–0.30, as is typical in BET plots. Calculated values of Q_m and $-(\Delta\bar{H}_m + \Delta\bar{H}_v)$ for the adsorbates are presented in Table I. In calculating Q_m and $\Delta\bar{H}_m$, the weight of minerals was assumed to be the same as the dry soil, since the organic content is only 1.9%.

The BET monolayer adsorption capacities for all compounds with dry Woodburn soil were established at relatively low P/P^0 ($\leq$0.18), except for benzene which occurred at $P/P^0 \simeq 0.23$. Observed capacities at high P/P^0 greatly exceed the monolayer values. Since adsorption on mineral matter should depend on the types of minerals (particularly, clays) (*9*, *10*), the calculated Q_m and $\Delta\bar{H}_m$ values represent weighted averages of all minerals in the soil. The $\Delta\bar{H}_m$ values (at $Q \leq Q_m$) are noticeably more exothermic than respective $-\Delta\bar{H}_v$ values by about 1.5–2.5 kcal/mol; these heat effects are consistent with the dominance of mineral adsorption with dry Woodburn soil.

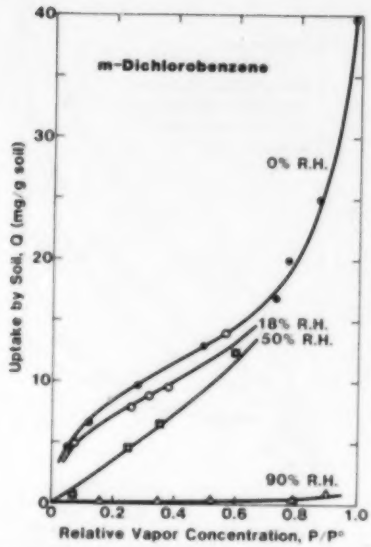

Figure 5. Vapor uptake of *m*-dichlorobenzene by Woodburn soil at 20 °C as a function of relative humidity.

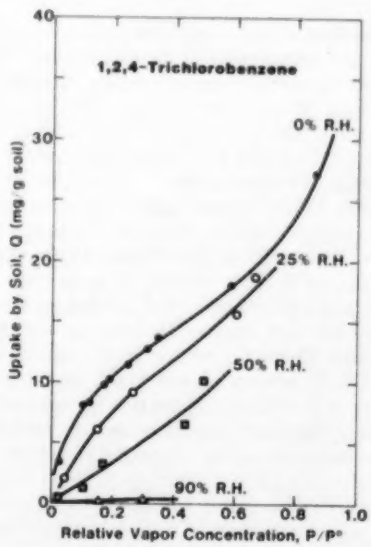

Figure 6. Vapor uptake of 1,2,4-trichlorobenzene by Woodburn soil at 20 °C as a function of relative humidity.

Consider now the effect of relative humidity on soil uptake of organic vapors. From the low uptake of solutes from water solution, one would expect the sorption of organic vapors to be strongly suppressed by water because of adsorptive competition on minerals. This effect should be most pronounced for low-organic-content mineral soils, since the amount sorbed through partition by soil-organic matter would be relatively insignificant. Figures 4–6 illustrate respectively the effect of humidity on the uptake of benzene, *m*-dichlorobenzene, and 1,2,4-trichlorobenzene by Woodburn soil. In spite of some uncertainty of the relative humidity (especially at 20% > RH > 85%), the progressive suppression of organic vapor uptake and resulting change in isotherm shape with an increase of RH are evident, as has been observed in the study of Call (*9*) on the uptake of ethylene dibromide by various soils.

In addition to the reduced capacities in the presence of water vapor, one notes that at RH $\geq$ 50% isotherms for the organic vapors become practically linear at $P/P^0 \leq 0.5$; this may again be attributed to adsorptive displacement

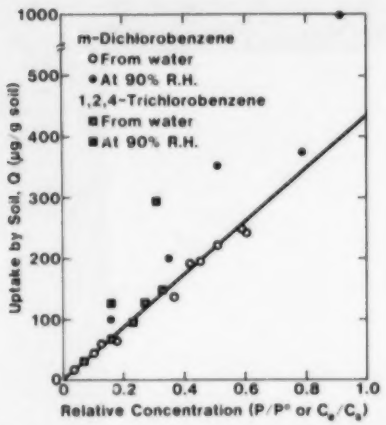

Figure 7. Comparison of the vapor uptake of *m*-dichlorobenzene and 1,2,4-trichlorobenzene by Woodburn soil at 90% RH (Q vs. P/P^0) at 20 °C with the corresponding uptake from water (Q vs. C_e/C_s) at 20 °C from ref 4.

of organic adsorbates by water at highly active mineral surfaces (this displacement is foreseen in Figure 2, where water exhibits significantly greater uptake at $P/P^0 = 0.5$ than organic vapors at $P/P^0 \leq 0.5$). As adsorption by soil minerals is further reduced by increasing amounts of humidity, uptake by partition into the soil organic matter would become more a controlling factor, enhancing the linearity of isotherms. At about 90% RH, the resulting isotherms of *m*-dichlorobenzene and 1,2,4-trichlorobenzene fall into a range close to the corresponding isotherms obtained from aqueous solution (Q vs. C_e/C_s), as illustrated in Figure 7. The benzene isotherm at ~90% RH shows much greater deviations from the aqueous-phase isotherm (by more than a factor 5 in capacity), which may stem partly from the inaccuracy of high humidity values in our experiments. Overall, the observed isotherms at ~90% RH sufficiently demonstrate the dominance of solute partition with the soil-organic phase in sorption from water, in contrast to mineral adsorption as the dominant effect when the soil is dry or contains only subsaturation humidities. Finally, while one cannot exclude the possibility of a small amount of residual linear adsorption on the mineral matter in the presence of water, it may be recalled that the partition effect is distinguished from linear adsorption on mineral matter by the fact that it increases with increasing organic matter content (*1*, *4*, *5*).

We now relate the preceding results to earlier studies on the uptake of organic compounds by soils and minerals from organic solvents and under some other system conditions. As noted, high uptake of parathion from hexane by dehydrated soils and clays (*6*, *14*, *15*) and its suppression by water (*6*, *14*) can be largely attributed to parathion adsorption on mineral matter and to subsequent competition of water for mineral adsorption. Our analysis is in keeping with Hance's finding (*16*) that a mineral-rich soil sorbs considerably more diuron from a (relatively nonpolar) petroleum solvent than from water, whereas the soil-organic matter shows the opposite effect. It also agrees with the finding by Spencer and co-workers (*17*, *18*) that the partial pressures of dieldrin and lindane incorporated into an originally dehydrated soil increase greatly when the soil is hydrated. Moreover, it predicts the failure of the soil to take up (nonionic) organic solutes such as parathion (*14*) from polar organic solvents, which reduce solute partition into organic matter by their good solvency and reduce adsorption on soil minerals because of their polarity. It explains the observation that nonpolar solvents (e.g., hexane) are less effective than polar solvents (e.g., acetone) for extracting organic pesticides from dry soils and that addition of water or polar solvents to hexane significantly improves the extraction efficiency (*19*).

In summary, the assumed roles of soil minerals and organic matter account both for the suppression of the soil uptake of organic vapors by water vapor and for the difference in sorption capacity from aqueous and organic solutions. Since the water content of surface soils can vary greatly with ambient humidity, the uptake of organic contaminants and pesticides by surface soils may be expected to be strongly influenced by ambient humidity.

Acknowledgments

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Registry No. Water, 7732-18-5; chlorobenzene, 108-90-7; *p*-dichlorobenzene, 106-46-7; *m*-dichlorobenzene, 541-73-1; 1,2,4-trichlorobenzene, 120-82-1; benzene, 71-43-2.

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